

Influence of blast furnace slag type on physical and mechanical properties of Portland cement

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Abstract. Physical properties, grain, chemical and mineral compositions of blast-furnace slags selected from the dumps of JSC 'EVRAZ Nizhny Tagil metallurgical plant' and PJSC 'Nadezhdinski Metallurgical Plant' were studied. Also, the same parameters of granulated blast-furnace slag of JSC 'Mechel-Materialy' currently used by cement plants in the Ural region as a mineral additive during Portland cement grinding were investigated. By chemical composition all of them are acidic. In contrast to granulated slag which mainly contains the vitreous phase dump slags are well crystallized and mainly contain the minerals okermanite, mervinite and monticellite. Dump slags have a Student's t-criterion of more than 15.0, i.e. they can be used as a mineral additive during Portland cement grinding. The introduction of 20 % of the studied slags reduces the water demand of Portland cement of joint grinding and accelerates the setting of the cement paste, reduces the bending and compression strength compared to the additive-free cement. Slag-containing cements after 7 and 28 days of hardening have similar values of compressive strength: 27.2–29.2 and 41.1–43.0 MPa respectively, they are normally hardening and have a strength class of 42.5. Chemical, physical and mechanical properties of these cements meet the requirements of Russian Standard 31108–2016.

1. Introduction

At cement plants in Russia granulated blast furnace slags (GBFS) are mainly used as a mineral additive in grinding Portland cement. According to Russian Standard 31108–2016 [1] Portland cements of types CEM II/A and CEM II/B can contain mineral additive, i.e. GBFS in an amount of 6–20 % and 21–35 % respectively as the main component. Granulated blast furnace slags used in the cement industry must meet the requirements of Russian Standard 3476–74 in terms of their composition and properties [2]. The introduction of GBFS increases water demand, lengthens setting, reduces the heat of cement hydration and improves resistance of cement stone to aggressive environments [3–5].

Recently the GBFS volumes of usage by cement plants has decreased significantly due to not only reduction in blast-furnace production of cast iron but also an increase of CEM I Portland cement use in monolithic construction [6]. In addition, the slag cost including transportation expenses increased to 1,000 Russian rubles (RUR) per ton while the average price of Portland cement is 4,000 RUR per ton. It is also necessary to take into account that the wet granulation slag has a high humidity (up to 25 %) and its drying requires a large fuel consumption which increases the cost of production of slag cements [7]. Taking into account these factors cement plants in the Ural region are investigating the feasibility of cheaper and more accessible rocks or man-made waste as a mineral additive for grinding cement such as fly ash from Reftinskaya State District Power Plant, ash-and-slag mix from Verkhnetagilskaya



State District Power Plant, and dump blast furnace slags (DBFS) from nearby metallurgical plants [8–11].

The aim of this work is to study the influence of the type of blast furnace slag formed at Ural metallurgical plants on the grindability and physical and mechanical properties of Portland cement.

2. Raw materials and research methods

The following raw materials were used in the work:

- cement clinker produced by CJSC ‘Nevyansky Tsementnik’ (Nevyansk) having a saturation coefficient $KN = 0.92$, silicate module $n = 1.9$, alumina module $p = 1.1$, mineral composition, %: 61.5 C_3S ; 13.1 C_2S ; 6.6 C_3A ; 15.7 C_4AF ; 0.3 CaO_{free} ;
- gypsum-anhydrite stone of the Ergachinsky Deposit containing 36.5 % $CaSO_4 \cdot 2H_2O$ and 60.0 % $CaSO_4$, which meets the requirements of Russian Standard 4013–82 [12];
- GBFS of JSC ‘Mechel-Materialy’, Chelyabinsk (sample 1);
- DBGS of JSC ‘EVRAZ Nizhny Tagil metallurgical plant’, Nizhny Tagil (sample 2);
- DBGS of PJSC ‘Nadezhdinski Metallurgical Plant’, Serov (sample 3).

Grain composition, bulk and true density of blast furnace slags were determined using standard methods and the specific surface area of crushed slag was determined using the air permeability method on the PSH-11M device.

Slag and clinker grindability was studied in a laboratory drum mill with ball loading when the ratio of the material (of fraction less than 5 mm)/grinding body is equal to 1/9, measuring the period of grinding to a residue on sieve No. 008 equal 5.0 %. The chemical composition of slag samples was determined according to Russian Standard 5382–91 [13], their X-ray phase analysis was performed on a Miniflex 600 diffractometer (Rigaku Technologies, Inc.) in the range of 2θ from 0 to 90° with automatic decoding using the ICDD PDF2 database (Japan).

The possibility of using of blast furnace slags as a mineral additive for Portland cement grinding was evaluated by their activity characterized by a statistical assessment of the significance of differences in compressive strength of samples with the addition of slag and quartz sand after steaming, i.e. by the Student's t-criterion, according to Russian Standard 25094–94 [14].

The hydraulic activity of slags with an MgO content of less than 10 % in accordance with Russian Standard 3476–74 was evaluated by the quality coefficient (K) calculated using the formula:

$$K = (CaO + Al_2O_3 + MgO) / (SiO_2 + TiO_2). \quad (1)$$

According to the values of the quality coefficient GBFS is classified to three grades: class I includes slags with a K of more than 1.65, class II – more than 1.45, and class III – at least 1.20. Also, the content of aluminum, magnesium, manganese and titanium oxides is limited in the blast furnace slags.

Grinding of Portland cement with 20 % slag and 6 % gypsum-anhydrite stone was carried out in a laboratory two-chamber ball mill. The grinding fineness, normal density and setting time of cement paste, specific surface area, bending and compression strength of cements with different types of slag were determined according to Russian Standard 30744–2001 [15] and the bending and compression strength of the cement mortar after steaming – according to Russian Standard 310.4–81 [16].

3. Results and discussion

3.1. Composition and properties of blast furnace slags

The results of determining the grain composition and density of samples of blast furnace slags are presented in table 1. It was found that the JSC ‘Mechel-Materialy’ GBFS contains mainly porous vitrified particles less than 5 mm in size (88.7 %). The slag sample of JSC ‘EVRAZ Nizhny Tagil metallurgical plant’ consists of up to 78.3 % broken stone with a 5–20 mm grains content and the sample of PJSC ‘Nadezhdinski metallurgical plant’ is represented by broken stone containing 92.0 % of particles of 10–40 mm in size. The slag of PJSC ‘Nadezhdinski metallurgical plant’ has the highest true density and the granulated slag of JSC ‘Mechel-Materialy’ has the lowest one.

Table 1. Grain composition and properties of blast furnace slags.

| Sample number | Slag manufacturer | The contents of the grains, %, on the sieve, mm | | | | Density, kg/m ³ | |
|---------------|--|---|-------|------|------|----------------------------|------|
| | | 20–40 | 10–20 | 5–10 | <5 | Bulk | True |
| 1 | JSC ‘Mechel-Materialy’ | – | 8.5 | 2.8 | 88.7 | 1250 | 2860 |
| 2 | JSC ‘EVRAZ Nizhny Tagil metallurgical plant’ | 2.1 | 35.6 | 42.7 | 19.6 | 1410 | 2980 |
| 3 | PJSC ‘Nadezhdinski metallurgical plant’ | 60.3 | 31.7 | 7.2 | 0.8 | 1320 | 2880 |

According to the chemical composition the studied blast furnace slags differ mainly in the content of calcium, magnesium and titanium oxides (table 2) and are acidic (basicity modulus less than 1). GBFS (sample 1) and dump blast furnace slag (sample 3) have a quality coefficient of more than 1.45 and belong to grade 2 and the dump blast furnace slag (sample 2) does not meet the requirements of Russian Standard 3476–74 in the amount of TiO₂ (more than 4 %) (table 3). The activity assessment of blast furnace slags by the Student's t-criterion showed that GBFS (sample 1) has the highest value (51.0) and dump blast furnace slag (sample 2) has the lowest value (15.7). Dump blast furnace slag (sample 3) has a t-criterion equal to 18.6. Thus, the studied dump blast furnace slags have a t-criterion value of more than 15.0, i.e. they can be used as a mineral additive when Portland cement grinding.

Table 2. The chemical composition of blast furnace slags.

| Sample number according to Table 1 | Chemical composition (mass %) | | | | | | | | |
|------------------------------------|-------------------------------|--------------------------------|--------------------------------|-------|------|-----------------|------|------------------|-------|
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | MnO | TiO ₂ | Other |
| 1 | 34.56 | 11.72 | 0.88 | 38.20 | 7.60 | 0.84 | 0.63 | 1.21 | 4.36 |
| 2 | 35.45 | 12.67 | 1.78 | 32.33 | 6.88 | 0.88 | 0.57 | 6.41 | 3.91 |
| 3 | 35.93 | 11.72 | 1.18 | 41.36 | 3.90 | 0.63 | 0.68 | 1.01 | 3.59 |

Table 3. Compliance of blast furnace slags properties with Russian Standard 3476 requirements.

| Indicators | Requirements of the standard for 1, 2, 3 grades | Actual values for slag samples | | |
|--|---|--------------------------------|-------|-------|
| | | 1 | 2 | 3 |
| Quality factor | ≥ 1.65; 1.45; 1.20 | 1.61 | 1.24 | 1.54 |
| Al ₂ O ₃ quantity (mass %) | ≥ 8; 7.5; – | 11.72 | 12.67 | 11.72 |
| MgO quantity (mass %) | ≤ 15 | 7.60 | 6.88 | 3.90 |
| TiO ₂ quantity (mass %) | ≤ 4 | 1.21 | 6.41 | 1.01 |
| MnO quantity (mass %) | ≤ 2; 3; 4 | 0.63 | 0.57 | 0.68 |

X-ray phase analysis of slag samples showed that GBFS (sample 1) is mainly represented by a glassy phase and a small content of the okermanite (2CaO·MgO·2SiO₂) and spinel (MgO·Al₂O₃) minerals (Figure 1, a). In contrast to granulated slag, both samples of dump blast furnace slags are well crystallized and contain the following minerals: okermanite, mervinite 3CaO·MgO·2SiO₂ and monticellite CaO·MgO·SiO₂ and the slag (sample 2) also contains perovskite and glass phase in a small amount (Figure 1, b, c). Thus, all three samples of blast furnace slag differ by the content of the vitreous phase and olivine group minerals which do not hydrate in the composition of Portland cement stone [17].

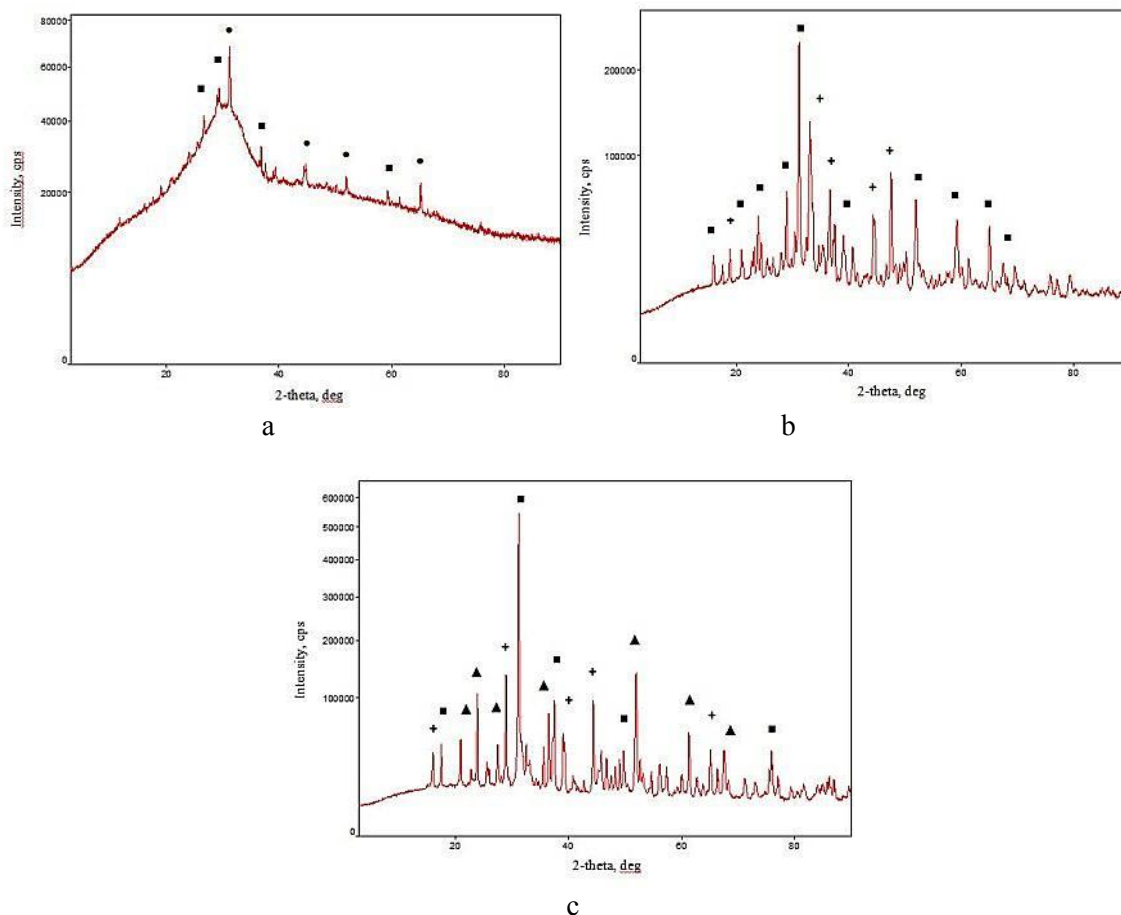


Figure 1. Diffraction pattern of samples of blast-furnace slag:

a – sample 1; b – sample 2; c – sample 3;

● – spinel; ■ – akermanite; + – merwinite; ▲ – monticelli.

3.2. Influence of slag additives on the properties of Portland cement

It is known that the structure and mineral composition of metallurgical slags affects not only their activity but also their grindability [18]. The grindability of all three samples of the studied blast furnace slags as well as Portland cement clinker was determined. It was found that slags are crushed much worse than clinker with a grinding time of 80 minutes. The samples can be ranked according to their grinding time: the longest is 180 minutes for sample 3, then sample 2 and sample 1 (GBFS) with grinding times of 120 and 140 minutes respectively.

Four compositions of Portland cement were prepared by joint grinding to study possibility of using of slags as a mineral additives: the first – without the addition of slag, from the second to the fourth – with 20 % of slags. The results of determining their physical and mechanical properties are presented in Table 4. It is found that the additive-free cement and Portland cement with GBFS are ground 15 % faster than the compositions containing samples of dump blast furnace slags. All cements had the same grinding fineness and similar values of specific surface area.

The cements obtained have different water demand: composition with the sample 3 slag has the lowest normal density equal to 26.4 %; cement with sample 2 slag has the highest normal density equal to 28.2 % having an increased specific surface area unlike other Portland cements. Compared to additive-free Portland cement all three samples of blast furnace slags accelerates the setting of cement paste and most strongly – with the introduction of DBFS of sample 2: initial setting time has decreased 1.8 times, the final setting – by 55 %. DBFS of sample 3 has the minimal influence on the cement setting.

Table 4. Results of physical and mechanical tests of Portland cements.

| Ce- ment sam- ple num- ber | Slag sam- ple num- ber | Fineness (mass %) | Specific surface area (m ² /kg) | Normal consis- tency of cement paste (%) | Setting time (min) | | The strength (MPa) | | | |
|---|------------------------------------|----------------------|---|--|--------------------|-------|--------------------------|-----|------------------------------|------|
| | | | | | | | Bending, after (days) | | Compression, after (days) | |
| | | | | | initial | final | 7 | 28 | 7 | 28 |
| 1 | – | 2.5 | 324 | 27.4 | 215 | 310 | 7.9 | 8.5 | 38.6 | 47.3 |
| 2 | 1 | 2.6 | 315 | 27.0 | 155 | 260 | 6.5 | 7.9 | 29.2 | 43.0 |
| 3 | 2 | 2.5 | 337 | 28.2 | 120 | 200 | 6.6 | 8.3 | 27.2 | 41.1 |
| 4 | 3 | 2.7 | 327 | 26.4 | 190 | 315 | 6.1 | 7.3 | 28.1 | 42.1 |

It was found that the introduction of all three samples of blast furnace slag into Portland cement in an amount of 20 % reduces the bending and compression strength compared to additive-free cement: cement with DBFS (sample 2) has minimal decrease of bending strength by 28 days of water hardening (by 2.4 %), and cement with DBFS (sample 3) has the largest strength decrease (by 16.4 %). However, all cements with slags have similar values of compressive strength after 7 and 28 days of hardening, i.e. 27.2–29.2 and 41.1–43.0 MPa respectively. By physical and mechanical properties all Portland cements containing blast furnace slag meet the requirements of Russian Standard 31108–2016; they are normally hardening and have a strength class of 42.5. In addition, they also meet its requirements in terms of chemical parameters (mass loss during ignition, insoluble residue, and chloride ion content).

4. Conclusions

The composition and properties of dump blast furnace slags of JSC ‘EVRAZ Nizhny Tagil metallurgical plant’ and PJSC ‘Nadezhdinski metallurgical plant’ and granulated blast furnace slag of JSC ‘Mechel-Materialy’ used by cement plants in the Ural region as a mineral additive for grinding Portland cement were studied. By chemical composition all of them are acidic. Unlike granulated slag, the dump ones are well crystallized and mainly contain such minerals as akermanite, merwinite and monticellite. Dump slags have a Student's t-criterion of more than 15.0, i.e. can be used as a mineral additive when grinding Portland cement. Blast furnace slags are milled by 1.5–2.2 times longer than Portland cement clinker; the titanium slag is especially harder to mill. The introduction of 20 % of the studied slags reduces the water demand of Portland cement of joint grinding, accelerates the setting of the cement paste, reduces the bending and compression strength compared to the additive-free cement. Slag-containing cements have similar values of compressive strength after 7 and 28 days of hardening, i.e. 27.2–29.2 and 41.1–43.0 MPa respectively. They are normally hardening and have a strength class of 42.5 and meet the requirements of Russian Standard 31108–2016 [1] by chemical, physical and mechanical properties.

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